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# ANALYSIS OF LIGHT-SCATTERING DATA FROM POLYMER SOLUTIONS

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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## ABSTRACT

An analysis was made of various factors affecting the analytical fitting of curves to a Zimm plot of light-scattering data from dilute polymer solutions. The use of a computer to completely fit the data analytically was not feasible. However, a procedure was developed whereby the computer calculates the points on the limiting tangent. This tangent is then extrapolated graphically to zero concentration. A computer program was written which incorporates this method.

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## SUMMARY

Because of the complex and time-consuming nature of the calculations and graphical construction of the Zimm plot, a computer program was written to handle all phases of the calculations and curve fitting. This program was applied to the light-scattering results obtained from the polystyrene-benzene system. The polystyrene samples were chosen to isolate the effects of data scatter and nonlinearity in the Zimm plot. The ability of the computer program to handle these effects was analyzed, the conclusion being that a purely analytical procedure was not adequate to handle these effects. Accordingly, the program was modified to make the curve fitting partly analytical and partly graphical. This procedure worked well with the polystyrene-benzene system, and the combination of experiment and analysis of light-scattering data suggested herein can be applied to other polymer-solvent systems with an expected accuracy of  $\pm 10$  per cent.

## INTRODUCTION

Certain mechanical properties of polymers are known to be related to the average molecular weight of the polymer (ref. 1). In general, an increase in average molecular weight leads to a desirable increase in the mechanical properties of the resin.

The absolute values of the weight average molecular weight  $\overline{M}_w$  or number average molecular weight  $\overline{M}_n$  can be determined, respectively, by light-scattering and colligative property measurements on dilute polymer solutions. Furthermore, if the absolute values of both  $\overline{M}_w$  and  $\overline{M}_n$  are known, the polydispersity (ratio of  $\overline{M}_w$  to  $\overline{M}_n$ ) of the polymer may be calculated. The mechanical properties of the resin are also related to the polydispersity.

Experimentally, light-scattering measurements are quite difficult, requiring careful and exacting attention to detail to achieve success. Once the technique has been mastered, however, it can be applied routinely over a wide range of polymer-solvent

systems to obtain  $\overline{M}_w$ .

The development of a procedure that would considerably simplify both the collection and reduction of light-scattering data was desired. A process was envisioned whereby the experimental data obtained in a run could be fed into a computer that would then reduce the data to give  $\overline{M}_w$  together with some estimate of the scatter of these data. It is also desirable to handle the data with a computer to avoid repetitive and time-consuming calculations. The design of a computer program to perform these calculations may be divided into two phases. In the first phase, the data are reduced to a form suitable for graphical determination of  $\overline{M}_w$ . In the second phase, a curve is fitted to the reduced data and used to obtain the value of  $\overline{M}_w$ . The main features of the program should be flexible input-output routines, graphic presentation of intermediate results by the computer's plotting capability, and simplicity in the handling and use of the program.

In addition to the development of the program, a careful analysis of the performance of the program in handling nonideal Zimm plots must be made because the equations developed for relating experiment to theory apply rigorously only in the ideal case.

Evans, Huglin, and Lindley (ref. 2) have recently written a program for statistically handling light-scattering data from polymer solutions. This program is written in a computer language unsuitable for most American computers. Furthermore, the program was not designed for simplicity of use and does not take into account a deviation from the simple  $\sin^2(\theta/2)$  dependence on the observation angle  $\theta$  of the light scattering. This deviation may be more important than the introduction of a squared term into the concentration dependence, which is the main feature of their program. A FORTRAN program (ref. 3) is available to reduce light-scattering data; however, disadvantages of this program are that it does not have a flexible input-output routine and does not treat the second phase of the calculation. Unfortunately, the curve-fitting procedure is not straightforward because even though, ideally, light-scattering theory predicts that the points should be on straight lines for low concentrations, this is only strictly true for a very small interaction between solvent and solute. In addition, because of the difficult experimental problems, the data may scatter, and it is not unusual to encounter several inconsistent measurements in a given run. It is of interest to investigate the effect of these inconsistent points on the curve fitting.

With these ideas in mind, a program was written using a simple least-squares curve-fitting procedure. The program was then tested by using a series of experimental runs on polystyrene dissolved in benzene. Two types of polystyrene samples were used: the first type included ARRO 160, and NBS 705 polystyrene with a  $\overline{M}_w$  of 179 000 and a polydispersity of approximately 1.0; the second type was NBS 706 with a  $\overline{M}_w$  of 258 000 and a polydispersity of 2.1. Benzene was chosen as a solvent because it is a "good" solvent for polystyrene, and it was expected to introduce some nonlinearity to the curves. The computer program and the results of tests made with the program are presented in

this report together with pertinent experimental details on the light-scattering photometer. All the symbols used in this report are defined in the appendix.

## EXPERIMENTAL PROCEDURE

The experimental details of light-scattering experiments are described in detail by Stacey (ref. 4), and the operating instructions for the light-scattering photometer are given in the instrument operating manual (ref. 5). In a typical experiment, polystyrene was dissolved in reagent-grade benzene to a concentration of about 1 gram per 100 milliliters of solution. This solution was then filtered in a pressure filter under an average nitrogen gage pressure of 10 psi ( $6.89 \times 10^4$  N/m<sup>2</sup>). The filter material used was a polyvinyl chloride filter with a 0.9-micron average pore size. Several lower concentrations were prepared by serial dilution of the original solution. The concentration of the solution in grams per milliliter was determined gravimetrically from a 10-milliliter aliquot. The light scattered from the solution was measured at  $90^\circ \pm \theta_i$ , where  $\theta_i = 45^\circ, 55^\circ, 65^\circ$ , and  $75^\circ$ . A measurement was also made at  $0^\circ$ . The light scattering was measured at wavelengths of 5460 and 4360 angstroms, and each measurement was repeated five times at each angle per concentration point. Thus, during a typical run, 450 measurements were made. The reduction of these points to obtain  $\overline{M}_w$  is the purpose of the computer program under examination herein. The working constant  $a$  and the narrow-slit correction factor  $r/r'$  were not truly constant and varied with time. The variation in  $a$  was not too important unless the mercury lamp output changed significantly or a new lamp was installed. However, the change in  $r/r'$  was more significant than that in  $a$ , amounting to as much as several percent per day. Furthermore,  $r/r'$  was difficult to measure accurately because solvent scattering, which is the least accurate quantity measured, enters significantly into the calculation of  $r/r'$ .

Beattie et al. (ref. 3) have estimated the total errors in a  $\overline{M}_w$  determination to be  $\pm 4$  percent for careful work under ideal conditions; however, these authors also state that a more realistic expected error is  $\pm 10$  percent.

In the present work, an accuracy of  $\pm 10$  percent is quite sufficient, and, accordingly, the method used for analyzing the data is judged acceptable if this accuracy is attained.

The polystyrene samples studied were NBS 705 ( $\overline{M}_w = 179\,000$ , polydispersity = 1.07), NBS 706 ( $\overline{M}_w = 258\,000$ , polydispersity = 2.1), and ARRO 160 ( $\overline{M}_w = 179\,000$ , polydispersity  $\sim 1.0$ ). These samples were chosen so that the effect of changes in  $\overline{M}_w$  and polydispersity on the analysis of the light-scattering data could be evaluated.

## BACKGROUND THEORY

The general theory of light scattering is well presented by Stacey (ref. 4) and need not be repeated herein. The measured quantity in a light-scattering experiment is the ratio of  $G(\theta, c)$ , the scattered light intensity at angle  $\theta$  and concentration  $c$  to  $G(0^0, c)$  the intensity of transmitted light at concentration  $c$ . The ratio  $G(\theta, c)/G(0^0, c)$  is measured for a number of angles and for a series of concentrations. From these ratios, the Rayleigh ratio  $R(\theta, c)$  is calculated according to equation (1) (refs. 5 and 6):

$$R(\theta, c) = \frac{\text{TDan}^2 \frac{R_w}{R_c}}{1.049 \pi h} \frac{r}{r'} \frac{\sin \theta}{1 + \cos^2 \theta} \frac{1}{(1 - R_n)^2 (1 - 4R_n^2)} \\ \times \left\{ \left[ \frac{G(\theta, c)}{G(0^0, c)} \right]_{\text{SOLN}} - \left[ \frac{G(\theta, c)}{G(0^0, c)} \right]_{\text{SOLV}} \right\} \\ - 2R_n \left\{ \left[ \frac{G(180^0 - \theta, c)}{G(0^0, c)} \right]_{\text{SOLN}} - \left[ \frac{G(180^0 - \theta, c)}{G(0^0, c)} \right]_{\text{SOLV}} \right\} \quad (1)$$

where  $R_n$  is a function of the refractive index of the light-scattering cell (in the present case,  $R_n = 0.039$ ), and it should be pointed out that  $R_n$  is not related to  $R(\theta, c)$ ; TD,  $h$ , and  $a$  are instrument constants;  $n$  is the refractive index of the solvent;  $R_w/R_c$  is a correction factor for the incomplete compensation of refraction effects for the polystyrene benzene system (for our system  $R_w/R_c = 1.036$  for 4360 Å light and 1.035 for 5460 Å light); the subscripts SOLN and SOLV refer to measurements made of the solution and pure solvent, respectively; and the quantity  $r/r'$  is a correction for the fact that the instrument was calibrated for absolute scattering by using wide-beam optics. When this instrument is used to determine the scattering at angles other than  $45^0$ ,  $90^0$ , and  $135^0$ , narrow-slit optics must be used. The Rayleigh ratio may then be related to the weight average molecular weight ( $\overline{M}_w$ ) of a polymer by the following equation:

$$\frac{Kc}{R(\theta, c)} = \frac{1}{\overline{M}_w P(\theta)} + 2B_2c + 3B_3c^2 + \dots \quad (2)$$

$$K = \frac{2\pi^2 n^2 (\Delta \bar{n})^2}{\lambda^4 N}$$

where  $\lambda$  is the wavelength of the scattered light, and  $N$  is Avogadro's number. The quantity  $\Delta \bar{n}$  is the specific refractive index increment of the polymer-solvent system and is given by the expression

$$\Delta \bar{n} = \frac{n - n_0}{c'}$$

where  $n$  is the refractive index of a solution of concentration  $c'$  (g/ml), and  $n_0$  is the refractive index of the pure solvent. To a good approximation,  $\Delta \bar{n}$  does not vary with  $c'$  for dilute polymer solutions. The quantity  $c$  is the concentration (g/ml) of the polymer solution under investigation,  $P(\theta)$  is the particle-scattering factor, and  $B_2$  and  $B_3$  are related to the second and third virial coefficients  $A_2$  and  $A_3$ , respectively, but are not necessarily equal to them.

Two methods are available for using equation (2) to interpret light-scattering data. In the first, the dissymmetry method, the scattering is measured at  $45^\circ$ ,  $90^\circ$ , and  $135^\circ$  for a series of concentrations. Two quantities are then calculated,  $R(90^\circ, c)$  and  $Z(c) = G(45^\circ, c)/G(135^\circ, c)$ , and  $Z(c)$  is called the dissymmetry. A plot is then made of  $R(90^\circ, c)$  against  $c$ , and  $R(90^\circ, 0)$  is then obtained by extrapolation. Similarly,  $Z(0)$  is obtained from a plot of  $1/Z - 1$  against  $c$  (ref. 7). However, from equation (2),  $[R(90^\circ, 0)]^{-1} = \bar{M}_w P(90^\circ)$ . Also, if a suitable model is chosen,  $[P(90^\circ)]^{-1}$  may be calculated as a function of  $Z(0)$ ; thus, if  $R(90^\circ, 0)$  and  $Z(0)$  are known,  $\bar{M}_w$  may be calculated. Problems arise in polymers if the polydispersity is high or if  $\bar{M}_w$  is high or if too large an interaction occurs between the polymer and the solvent, because then the plot of  $R(90^\circ, c)$  against  $c$  is not linear. This situation can sometimes be remedied by working at low concentrations. In practice, it is not advisable to use the dissymmetry method for  $\bar{M}_w$ 's much over 500 000 or for polymers with a high polydispersity.

The second method, called the Zimm method after the man who first suggested it (ref. 8), makes use of the fact that  $[P(0^\circ)]^{-1} = 1$ . Zimm adopts the simplified equation

$$\frac{Kc}{R(\theta, c)} = \frac{1}{\bar{M}_w P(\theta)} + 2A_2 c \quad (3)$$

and shows that  $A_2$  does not depend on  $c$ . He assumes that

$$[P(\theta)]^{-1} = 1 + \bar{K} b^2 \nu \sin^2\left(\frac{\theta}{2}\right) \quad (4)$$



where  $\bar{K}$  is a constant,  $b$  is a characteristic length associated with a given polymer system,  $\nu$  is the degree of polymerization, and  $b^2\nu$  is the root-mean-square end-to-end chain distance. Higher order terms of the order of  $\sin^4(\theta/2)$  have been omitted from equation (4) (according to Zimm). If a plot, commonly called a Zimm plot (see fig. 1), is then made of  $R(\theta, c)$  against  $\sin^2(\theta/2) + kc$ , where  $k$  is simply a scale factor chosen to give a convenient separation of points, the points fall on a series of vertical lines with each line corresponding to a given concentration. If equations (3) and (4) are accepted, these lines should be linear and parallel. The lines are then extrapolated to zero angle, and the points  $R(0^\circ, c)$  are obtained. These points then make up one of the limiting tangents to the surface described by equation (4). The limiting tangent may be linear, but there are some indications (ref. 9) that the surface is concave. In any case, knowledge of the linearity of the surface at low concentrations is important in making the extrapolation properly. Some factors that affect the linearity of the surface are polydispersity,  $\bar{M}_w$ , and the extent of the interaction between the polymer and its solvent. In general, high polydispersity, high  $\bar{M}_w$ , and a large interaction between polymer and solvent (i. e., for a "good" solvent) tend to make the surface more concave. A further complication has been introduced by Flory and Bueche (ref. 10) who, working with the Gaussian smoothed-density model for a polymer chain, have proposed that  $B_2$ ,  $B_3$ , etc., from equation (2) have some angular dependence and, hence, are not equal to the second, third, etc., virial coefficients as assumed by Zimm. This effect, which is expected to be more pronounced for good solvents, casts doubt on the simple  $\sin^2(\theta/2)$  angular dependence of  $R(\theta, c)$ . This effect could be observed in the deviation from linearity of points on the Zimm plot taken at a given concentration. This deviation has been observed for some polymer-solvent systems (ref. 11). Because of these complications, care must be exercised in the interpretation of light-scattering results from a new polymer-solvent system.

## COMPUTER PROGRAM

### General Remarks

Although the primary emphasis of this report is on an analysis of the feasibility of using a computer to analyze light-scattering data, a brief description of the program and some of its options are of interest. The computer program has been designated as ZIMM for obvious reasons.

The main purpose of the program is to calculate Rayleigh ratios and analyze these by the method of Zimm (ref. 8) using a least-squares curve-fitting procedure. However, two other optional features of the program are worthy of mention. The first option allows the computer to plot the Zimm plot, which is important because it allows the pro-

grammer to identify Rayleigh ratios that are not in agreement with the rest of the data. This feature is quite useful in identifying errors in the data, typographical errors in the card punching, or Zimm plots in which the points do not fall on straight lines. The second option allows the program to be used to analyze the data according to the dissymmetry method. The program automatically recognizes this option when the number of angles at which the scattering is measured is less than three (not counting the zero angle). This subroutine calculates the dissymmetry and the turbidity at each concentration and prints them out. The programmer must then plot these quantities against concentration and extrapolate to zero concentration. When  $\overline{M}_w$  is not too high, this procedure is preferred.

The program itself is organized into two phases. In the first phase, the light-scattering data are read in and used to calculate Rayleigh ratios. In the second phase, these ratios are analyzed according to either the Zimm or the dissymmetry method. More details on these phases are given in the following two sections.

## Phase I

An attempt has been made in the first phase to introduce maximum flexibility into the input procedure. Thus, the upper index of all DO statements is an integer variable. These variables are set according to the number of concentrations, number of angles, and number of repetitive readings involved in a particular run. Other input data, such as instrument constants and symmetry correction factors, are also read in at this time. The Rayleigh ratios ( $R(\theta, c)$ ) are then calculated as a function of angle  $\theta$  and concentration  $c$  according to equation (1) and stored in the two-dimensional array GC. The quantities  $Kc/R(\theta, c)$  are then calculated and stored in the two-dimensional array GG for use in later sections of the program. Similarly, the function  $\sin^2(\theta/2) + Kc$  is calculated and stored in the two-dimensional array X. At this time the plotting subroutine may be called to construct a Zimm plot using X and GG. The arrays GG and X are printed out to facilitate the location of inconsistent points.

Also at this time, the option to call the dissymmetry subroutine is automatically implemented if the number of angles is equal to three. This subroutine calculates the turbidity  $\tau$  for each concentration according to the following equation:

$$\tau(c) = \frac{16 T D a n^2}{3(1.049)h} \frac{R_w}{R_c} \frac{G(90^\circ, c)}{G(0^\circ, c)} \quad (5)$$

Then the function  $Hc/\tau(c)$  is calculated for each concentration with

$$H = \frac{32\pi^2 n^2 (\Delta n)^2}{3\lambda^4 N} \quad (6)$$

The symbols in these equations have been previously defined in the BACKGROUND THEORY section. It is important to note that both  $H$  and  $k$  are defined for specific wavelengths and that the program is set up to calculate these quantities for the specific wavelengths of 5460 and 4360 angstroms as these are the working wavelengths of the photometer. However, the program may be easily modified to take into account other wavelengths. If the dissymmetry option is exercised, the program exits immediately on completion of this option.

## Phase II

In the second phase of the program, points corresponding to one constant concentration ( $c_i$ ) are assumed to fall on a straight line

$$\frac{Kc_i}{R(\theta, c_i)} = \alpha(c_i) + \beta \sin^2\left(\frac{\theta}{2}\right) \quad (7)$$

where  $\alpha(c_i)$  is a constant for any concentration. The constants  $\alpha(c_i)$  and  $\beta$  are calculated by a least-squares procedure, and the points on the limiting tangent  $Kc_i/R(0^0, c_i)$  are determined. These points, in turn, are fitted by a least-squares procedure, and the point at zero angle and zero concentration is determined;  $\bar{M}_w$  (from eq. (3)) is then equal to the reciprocal of this value. In determining the least-squares fit, an alternative procedure was introduced to ignore some points at high concentration and to partly eliminate the effect of line curvature. However, this procedure did not work well and was abandoned because not enough points remained to give a good statistical fit. Also printed out is the slope of the limiting tangent (from which  $A_2$  may be calculated), the variance of  $(\bar{M}_w)^{-1}$ , and the slope of the line  $c = 0$  from which the root-mean-square end-to-end chain distance may be calculated.

In view of the discussion in the BACKGROUND THEORY section, it may seem unlikely to expect the data to fall on straight lines. In practice, however, this is quite often the case, and even when it is not the case, it may be possible to correct the results in a simple manner. This matter is covered more thoroughly in the RESULTS AND DISCUSSION section.

## RESULTS AND DISCUSSION

Several sets of data obtained on various polystyrene samples dissolved in benzene were processed in ZIMM, and the results are given in tables I and II. Table I, which gives the results for the ARRO 160 sample, is arranged in three sections according to whether or not the  $r/r'$  used in the calculations was 1.4, 1.5, or 1.6. The  $\overline{M}_w$  designated as  $\overline{M}_w(\text{prog})$  was calculated by the program. The value  $\overline{M}_w(\text{graph})$  was obtained by the graphical extrapolation of the limiting tangent to zero concentration. This limiting tangent was obtained from intermediate printout from ZIMM. Table II lists the results obtained from a study of the NBS samples and is organized in a manner similar to table I.

Two important factors affecting nonlinearity in Zimm plots are polydispersity and solvent-polymer interaction. The polystyrene samples investigated were chosen to evaluate these two effects. The first was the ARRO low polydispersity ( $\sim 1.0$ ) and moderately low  $\overline{M}_w$ . This sample was expected to give fairly linear Zimm plots although the choice of benzene as the solvent might introduce some curvature. The second sample was NBS 706. This sample, with its higher molecular weight and higher polydispersity was expected to introduce some curvature into the Zimm plot. The study of NBS sample 705 with similar specifications as the ARRO sample was conducted to check the results obtained with the ARRO sample.

Another facet of the testing procedure was the evaluation of the effect of data scatter in determining the  $\overline{M}_w$ . This effect is potentially important because straight lines are fitted to only nine points at each concentration, thus, one or two inconsistent points could appreciably affect the extrapolation of this concentration to zero angle. Furthermore, in a typical run, only five concentrations are used, thus, if one limiting tangent point is in error, a serious error in  $\overline{M}_w$  may result. Therefore, it is essential to determine just how sensitive ZIMM is to data scatter.

The effect of each of these two sources of error may be separated by noting that most of the error in determining  $\overline{M}_w$  on the ARRO sample (table I) is caused by scatter in the data. The effect of  $r/r'$  was also evaluated by calculating  $\overline{M}_w$  using three different values of  $r/r'$ . In general, the percentage change in  $\overline{M}_w(\text{prog})$  was about equal to the percentage difference in the values for  $r/r'$  used in the calculation.

All values of  $r/r'$  measured in this study fell within the range  $1.4 \leq r/r' \leq 1.6$ , with most of them clustering about the value of  $r/r' = 1.5$ . This value agrees with other values reported in the literature (ref. 3). Moreover, all three values of  $r/r'$  yielded values of  $\overline{M}_w$  that were within 10 percent of 179 000. Figure 2 shows the limiting tangents calculated for run 4A using both 1.4 and 1.6 for  $r/r'$ . As can be seen, the lines are nearly parallel with approximately the same percent separation between them as between 1.4 and 1.6. Thus, it appears that deviations of  $r/r'$  affect the calculated

$\overline{M}_w$  in a linear manner, as expected. Figure 2 is typical of the results obtained by varying  $r/r'$ . In the experiments, the ratio  $r/r'$  seems to be the limiting factor in the accuracy of the Rayleigh ratio measurements. In work that requires an accuracy greater than  $\pm 10$  percent, it may be necessary to measure  $r/r'$  before each run. As expected, the ARRO-benzene and the NBS 705-benzene systems gave linear Zimm plots when the highest concentrations used were below about 1 percent. Therefore, the high values for  $\overline{M}_w(\text{prog})$  observed in table I resulted from scatter in the data. This result could be corrected by plotting the limiting tangent and graphically extrapolating it to  $c = 0$ . This procedure is quite simple since the program prints out the required values of  $R(0^0, c)$  and  $c$  as a table of intermediate results. Also, the experimenter is allowed to exercise judgment in neglecting certain points. The values of  $\overline{M}_w(\text{graph})$  were obtained by this procedure. As can be seen from figure 3, one point shows a large deviation from a straight line drawn through the other four points. If this point is included in the least-squares curve-fitting procedure, a large deviation in  $\overline{M}_w$  is obtained (compare  $\overline{M}_w(\text{prog})$  and  $\overline{M}_w(\text{graph})$  in table I for run 2A and  $r/r' = 1.5$ ). The value of  $[\overline{M}_w(\text{prog})]^{-1}$  is shown in figure 3 as a solid symbol. The experimenter, by neglecting the inconsistent point or by repeating the measurements needed to obtain this point, may exercise some control of the curve-fitting procedure used to obtain  $\overline{M}_w$ . In most cases, this control provides a satisfactory method dealing with the scatter normally encountered in light-scattering data. This conclusion is supported by the data in tables I and II.

In table I, the values of  $\overline{M}_w(\text{graph})$  (with  $r/r' = 1.5$ ) all fall within  $\pm 6$  percent of 179 000 except for run 2A. Table II shows that the values obtained for  $\overline{M}_w(\text{graph})$  of NBS 705 are within  $\pm 4$  percent of 179 000.

Correcting for nonlinearity of the Zimm plot is more difficult. The limiting tangent plotted for a scattering run on NBS sample 706 is shown in figure 4. As expected, the graph shows slight curvature. Even this small deviation from linearity can cause considerable error in  $\overline{M}_w$  as seen from the values of  $\overline{M}_w(\text{prog})$  in table II calculated for a light-scattering determination on NBS 706 with no allowance for curvature. Again the values of  $[\overline{M}_w(\text{prog})]^{-1}$  are shown as solid symbols in figure 4. However, this deviation was quite satisfactorily corrected by graphic extrapolation of the limiting tangent, as seen by the values of  $\overline{M}_w(\text{graph})$  given in table II. From these results, it seems likely that deviation from linearity may be at least partly corrected for by the graphical extrapolation procedure. Although these results were obtained for only one polymer-solvent system, they strongly suggest that attention should be directed to the behavior of the limiting tangent when curves are fit to a Zimm plot by a mathematical method. A simple straight-line least-squares procedure appears to be adequate for fitting the lines of constant concentration, but the points on the limiting tangent should be treated by a graphical procedure. However, it is appropriate to inject a note of caution at this point in that this procedure may not be valid for polymer-solvent systems in which a large

deviation from linearity occurs. Therefore, when dealing with an unfamiliar polymer-solvent system, it is advisable to plot the entire Zimm plot and compare the results obtained with those obtained from graphical extrapolation of the limiting tangent. Also, light scattering should be investigated at low concentrations because often nonlinearity in the Zimm plots can be eliminated by decreasing the contribution of  $c^2$  and higher order terms to  $R(\theta, c)$ .

## CONCLUDING REMARKS

The experimental procedure developed in this investigation, utilizing the light-scattering method and a light-scattering photometer, yielded weight average molecular weights accurate to  $\pm 10$  percent. The accuracy is somewhat dependent on the polymer-solvent system under study. The computer program presented herein proved flexible enough in input-output procedure to handle extensive changes in the data format. This flexibility is desirable in handling light-scattering data. The program reliably calculates weight average molecular weights when the Zimm plot is close to linear. When it deviates from linearity, the data cannot be fitted by straight lines. However, this deviation could be at least partly corrected for by the graphic extrapolation procedure, which is usually sufficient to obtain good results, as shown by the data for the NBS polystyrene 706 sample. Another factor that may introduce error is that the effect of one or two inconsistent points in the Zimm plot seems to be considerably magnified. However, this source of error may also be eliminated by the same method of graphic extrapolation. For these reasons, making a plot of the points involved in the limiting tangent line is recommended. If the polymer-solvent system is amenable to the use of the dissymmetry method, the program recognizes this from the form of the input data and automatically switches to the dissymmetry subroutine. No problems have been encountered in the use of this subroutine. The most critical experimental parameter was the factor  $r/r'$ , which must be continually determined if an error of less than  $\pm 10$  percent is desired.

Lewis Research Center,  
National Aeronautics and Space Administration,  
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## APPENDIX - SYMBOLS

$A_m(m=2, 3, \dots)$	second, third, etc., virial coefficients
$a$	instrument working constant
$B_m(m=2, 3, \dots)$	constants related to the second, third, etc., virial coefficients defined in eq. (2)
$b$	characteristic segment length
$c$	concentration, g/ml
DO	FORTTRAN computer language statement
GC	array used in ZIMM to store intermediate results
GG	array used in ZIMM to store calculated Rayleigh ratios
$G(\theta, c)$	intensity of light scattered at angle $\theta$ and concentration $c$
$H$	constant defined in eq. (6)
$h$	width of light-collimating diaphragm
$K$	constant defined in eq. (2)
$\bar{K}$	constant defined in eq. (4)
$k$	Zimm plot scale factor
$\bar{M}_n$	number average molecular weight
$\bar{M}_w$	weight average molecular weight
$\bar{M}_w(\text{graph})$	$\bar{M}_w$ calculated by graphical extrapolation
$\bar{M}_w(\text{prog})$	$\bar{M}_w$ calculated by ZIMM
$N$	Avogadro's number
$n$	refractive index of solution
$\Delta\bar{n}$	specific refractive index increment of polymer-solvent system
$n_o$	refractive index of solvent
$P(\theta)$	particle-scattering factor
$R(\theta, c)$	Rayleigh ratio
$R_n$	function of refractive index of light-scattering cell
$R_w/R_c$	correction factor for incomplete compensation of refraction effects
$r/r'$	correction factor from wide beam to narrow beam optics

TD	instrument correction factor
X	array used in ZIMM to store $kc + \sin^2(\theta/2)$
Z(c)	dissymmetry
ZIMM	computer program discussed in this report
$\alpha(c), \beta$	constants defined by eq. (7)
$\theta$	scattering angle
$\lambda$	wavelength of scattered light
$\nu$	degree of polymerization
$\tau(c)$	turbidity



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TABLE I. - WEIGHT AVERAGE MOLECULAR WEIGHT OF ARRO 179 SAMPLES  
CALCULATED BY VARIOUS METHODS

Run	Wave-length, $\lambda$ , $\text{\AA}$	Weight average molecular weight $\overline{M}_w$ calculated by -					
		ZIMM program	Graphical extrapolation	ZIMM program	Graphical extrapolation	ZIMM program	Graphical extrapolation
		Correction factor from wide beam to narrow beam, $r/r'$					
		1.4		1.5		1.6	
1A	4360	$1.62 \times 10^5$	$1.61 \times 10^5$	$1.64 \times 10^5$	$1.86 \times 10^5$	$1.79 \times 10^5$	$2.02 \times 10^5$
1B	5460	1.85	1.61	1.94	1.89	2.10	2.22
2A	4360	2.51	1.58	2.59	1.59	2.77	1.83
2B	5460	4.31	1.88	4.63	1.89	4.88	2.02
3A	4360	1.70	1.56	1.76	1.76	1.88	1.87
3B	5460	1.71	1.59	1.87	1.87	1.94	1.90
4A	4360	1.74	1.68	1.77	1.77	1.93	1.92
4B	5460	1.73	1.72	1.81	1.81	1.96	1.97
5A	4360	1.87	1.80	1.90	1.82	2.07	1.98
5B	5460	1.90	1.80	2.07	1.89	2.16	2.00

TABLE II. - WEIGHT AVERAGE MOLECULAR WEIGHT OF NBS  
SAMPLES CALCULATED BY VARIOUS METHODS

Sample	Wave-length, $\lambda$ , $\text{\AA}$	Weight average molecular weight, <sup>a</sup> $\overline{M}_w$	Weight average molecular weight $\overline{M}_w$ calculated by -	
			ZIMM program	Graphical extrapolation
			Correction factor from wide beam to narrow beam, $r/r' = 1.5$	
NBS 705	4360	$1.79 \times 10^5$	$1.75 \times 10^5$	$1.85 \times 10^5$
NBS 705	5460	1.79	1.71	1.75
NBS 706	4360	2.58	3.15	2.62
NBS 706	5460	2.58	3.02	2.65

<sup>a</sup>As measured by NBS.

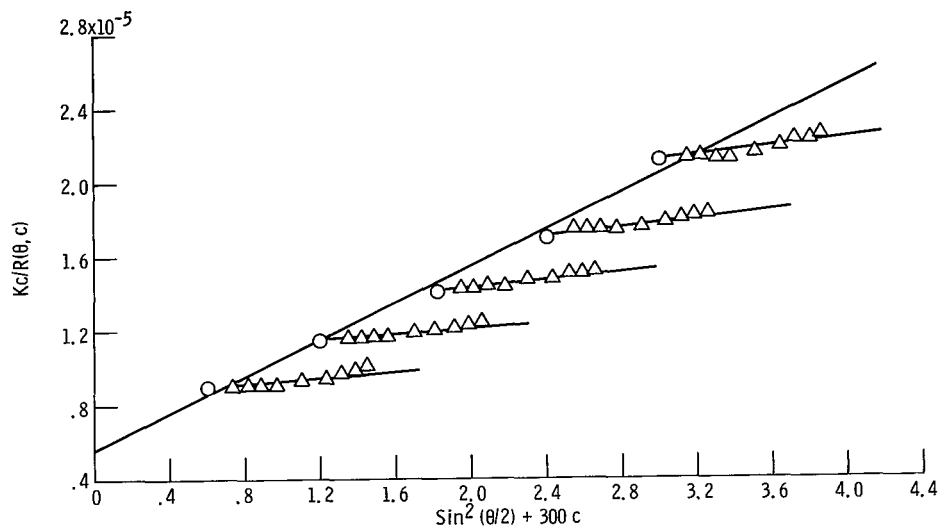


Figure 1. - Typical Zimm plot for polystyrene-benzene system.

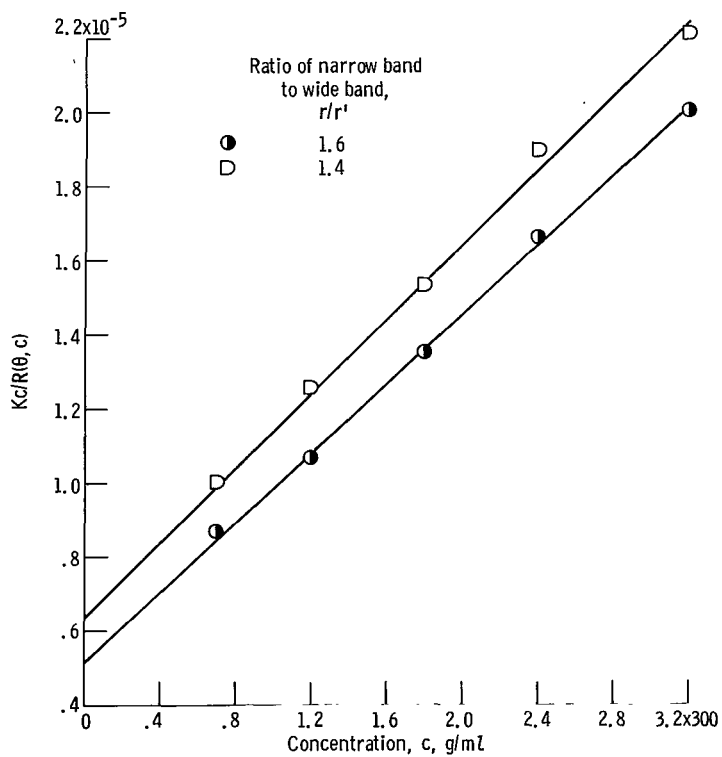


Figure 2. - Limiting tangents calculated for run 4A of ARRO sample showing effect of varying ratio of narrow band to wide band.

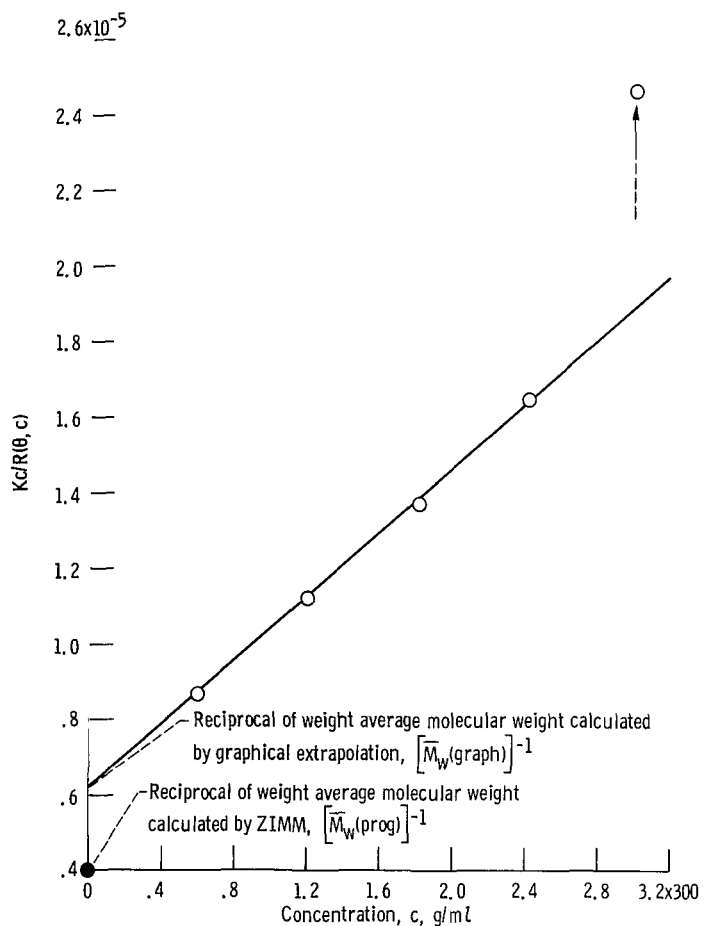


Figure 3. - Limiting tangent for run 2A of ARRO sample showing effect of an inconsistent point on determination of weight average molecular weight. Ratio of narrow beam to wide beam, 1.5.

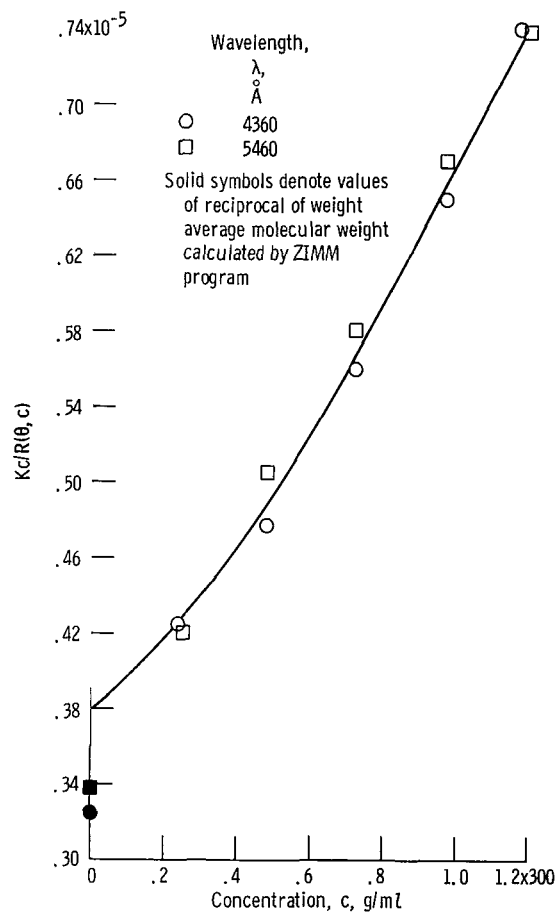


Figure 4. - Limiting tangent calculated for NBS 706 sample showing effect of nonlinearity. Weight average molecular weight, 258 000; ratio of narrow beam to wide beam, 1.5.

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